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X-RAY SCATTERING BY POINT DEFECTS

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I.- Principle of the method

The scattering of X-Rays by a perfect crystal outside of the Bragg-Laue diffraction directions is due to the thermal agitation scattering and the incoherent Compton scattering. These scatterings tend respectively towards a small value and zero when the scattering angle tends towards zero.

If the crystal contains point defects, as isolated vacancies or interstitials, theory shows that a scattering arises proportional to the square of difference of the scattering factor of the cell containing the point defect and of the normal unit cell. For instance, let us suppose that isolated vacancies producing negligible lattice distorsions are dispersed at random in a simple crystal containing one atom of scattering factor F per unit cell, then the scattering power per unit cell is :

$$I = C F^2 \qquad (1)$$

if C is the proportion of missing atoms. This formula shows that the scattering characteristic of point defects has the same variation as F^2, i.e. it is maximum at zero angle and decreases slowly and monotonically with increasing angle. In fact, it is practically constant for scattering angles below 10° with the radiation Cu Kα. Furthermore, its value is very weak because the concentration of vacancies is always small.

If the defect is not punctual, the scattering becomes more and more concentrated around the direction of the primary beam as the size of the defect increases and, on the other hand, the maximum value of the scattering at zero angle increases (Fig. 1). Let us suppose that the C vacancies are grouped into small aggregates of n vacancies dispersed in the lattice (which is supposed to remain little distorted), the maximum scattering is $I_0 = \frac{C}{n} \cdot n^2 F^2 = n(C F^2)$. (2)

Another possible application of the method is the study of a completely disordered solid solution. If the alloy composed of two atoms of scattering factors F_A and F_B, in proportion C_A and C_B ($C_A + C_B = 1$) is completely disordered, the scattered intensity per unit cell is given by the 'Laue formula' :

$$I = C_A C_B (F_A - F_B)^2 \quad . \qquad (3)$$

This 'Laue monotonic' scattering is maximum at zero angle and remains practically unchanged for angles below 10^{o}. It is approximately equal to $C_B(F_A - F_B)^2$ if $C_B \ll C_A$ and its maximum value would be $\frac{1}{4}(F_A - F_B)^2$ if there exists an equiatomic solid solution perfectly disordered.

If the observed scattering is not equal to the calculated value by the Laue formula, that means that the B atoms are not randomly dispersed in the solid solution. If the scattering in the small angle region is larger,it is an indication of the clustering of B atoms. On the other hand, if the intensity of scattering is smaller than the Laue monotonic scattering, there is a tendency towards ordering between the A and B atoms. In addition, in the first case, the intensity of scattering should be decreasing with angle if the clusters are not too small and, in the second case, diffuse maximums may be observed at the position of possible superlattice diffraction spots.

These examples show that the measurement in absolute value of the scattered intensity at small angle may give interesting information about point defects in a crystal. The measurements at small angles are especially advantageous because the other causes of scattering (Compton and thermal agitation) are at a minimum in this domain, and one can hope to detect a very weak scattering. But to exploit fully the possibilities of this method, it is necessary to have an apparatus of sufficient sensitivity.

II.- Description of the apparatus

The main problem in ordinary X-Ray diffraction studies is to determine a curve of the intensity as a function of angle, which, in general, may contain more or less sharp peaks. Therefore the accuracy of determination of the scattering angle is considered as an essential condition. But in our special problem, we consider only samples where the scattering is independent of angle or very slowly varying. In these particular cases, it is therefore unnecessary to limit the solid angle which defines the diffracted beam received by the counter at a very small value as in the ordinary diffractometer. Furthermore, the scattering we are looking for is isotropic : hence we can increase the aperture angle of the measured scattered beam and so increase considerably the sensitivity of the receiver whereas the angular resolving power is very much decreased.

The main features of the apparatus built by A.M. Levelut according to these ideas are the following. The beam irradiating the sample is crystal-monochromated and it converges on a small focus. For this purpose, the monochromator (a LiF lamella) has been given a double curvature : the lamella (.2 mm thickness) is pressed and glued against a concave toroïdal metallic surface whose principal radii are $R_1 = 350$ mm and $R_2 = R_1$, $\sin^2 \theta_0 = 51.3$ mm , θ_0 being the Bragg angle for the (200) planes and Cu Kα. The monochromatic reflected beam has an aperture of 1° and 1°15' in the two directions; its intensity is not quite uniform because of the defects of the LiF crystal and perhaps irregularities of curvature. But the actual focus is a small rectangle of .5 × 1 mm. The sample is placed on the reflected beam between the monochromator and the focus at about 35 mm from this focus. Thus its irradiated surface is of the order of .7 × 1.5 mm and its thickness is adjusted at $\frac{2}{\mu \rho}$ to $\frac{3}{\mu \rho}$ (μ, mass absorption coefficient; ρ, density) : it is higher than the thickness ($1/\mu \rho$) giving the maximum scattered intensity, but the ratio of the scattered intensity to the parasitic radiation coming from the monochromator is reduced.

The direct beam is stopped by a beam-catcher and the scattered beam is defined by a ring-shaped slit, the axis of which is the average incident ray (Fig. 2). The diffracted beam is limited by two cones of semi-apex angle, ε and $\varepsilon + \Delta \varepsilon$. By using different pairs of screens and also different sample to screen distances, ε may be fixed at a value comprised between 2° 40' and 6° 20' and $\Delta \varepsilon$ fixed at 30' or 40'.

The receiver must be able to count any photons passing through the annular slit with the same efficiency : it must thus have an uniform sensitivity over a front surface of nearly 40 mm diameter. This is possible by using a large scintillator crystal placed before a photomultiplier. It has been verified that the sensitivity was constant over the effective window. It is absolutely necessary, to reach the desired sensitivity, to eliminate as far as possible any stray radiation in the beam reaching the counter. Therefore the scintillator and the sample are placed in an evacuated box (Fig. 3) to avoid air scattering by the direct beam. The box is closed by a perspex window scintillator and the P.M. is situated in air outside the box. A system of slits (F_1 and F_2) before the sample are carefully adjusted to stop the rays scattered by the monochromator without touching the main primary beam.

A new apparatus built on the same principles is now in construction. The adjustment of the screens is made easier and the sample can be heated or cooled to liquid N_2 temperature.

III.- Limit of the sensitivity for detection of weak scattering

The limiting sensitivity depends mainly on the level of the background of the pulses registered by the counter when there is no sample on the incident beam : it is the sum of the proper background of the counter and of the pulses due to stray radiations in a blank experiment. We shall admit that the smallest measurable scattered intensity is equal to the background intensity, E_p. Let I be the scattering power per atom of the sample, S and x the surface and thickness of the irradiated volume, μ and ρ, the mass absorption coefficient and the specific mass, A, the atomic mass. I_0, intensity of the incident beam, is equal to E_0/S, E_0 being the energy in the incident beam.

In the solid angle Ω of the beam entering the counter, one single free electron emits an energy equal to : $7.9 \times 10^{-26} \Omega \frac{E_0}{S}$. Therefore the scattered intensity produced by the sample is :

$$E = 7.9 \;\; 10^{-26} \Omega \frac{E_0}{S} I . \frac{S \, x \, \rho}{A/6.06 \;\; 10^{23}} \exp(-\mu \, \rho \, x) \; .$$

For the value $x = \frac{1}{\mu \, \rho}$, the minimum detectable scattering power is :

$$I_m = \frac{70}{\Omega} \frac{E_p}{E_0} A \, \mu \quad .$$

For our present apparatus, $\frac{E_p}{E_0} = 10^{-6}$ and Ω may be $2 \; 10^{-3}$; for isolated vacancies, I is given by Eq.(1) and the minimum concentration of vacancies which can be detected is found $2.7 \;\; 10^{-3}$ for Al; $1.3 \;\; 10^{-3}$ for Cu; $3.7 \;\; 10^{-3}$ for Ag; $2.4 \;\; 10^{-3}$ for gold, etc.

In fact, the measured scattering has to be corrected for Compton and thermal agitation scattering which is equivalent to the scattering power of a few thousandths of vacancies. The most precise method is to compare two crystals of the same nature with and without vacancies, and also to make the measurement at a low temperature. The most interesting consequence of this calculation is to give an order of magnitude of the available sensitivity. It is likely that progressive improvements of the apparatus may increase slightly its performance and it must be noted that there is an important progress in comparison with a conventional diffractometer.

IV.- Some examples of studies of point defects

These examples have been chosen to test the possibilities of the apparatus and the experimental method in different kinds of problems.

1) Verification of the Laue equation for disordered solid solutions

We have tried to prepare a solid solution to see if a perfectly disordered solid solution can exist in equilibrium. Such experimental tests of the Laue equation had not been reported.

In the aluminium-based alloys, Al-Ga is the most favourable system, because the limit of solubility of Ga in Al is high (15 at. o/o) and the difference between the atomic numbers is large. For a Al-3.4 % Ga alloy homogeneized at high temperature and slowly cooled, the agreement is very satisfactory between the measured scattering and the calculated value corrected for Compton and thermal scattering : the Compton scattering has been calculated from the theoretical values given in International Crystallographic Tables and the thermal scattering has been assumed to be equal to that of pure aluminium (Fig. 4).

A similar good agreement has been found for an Al-.45 % Cu alloy after a long annealing at 400° C, in the region of homogeneous solid solution and quenched at room temperature. This sample has been compared to pure aluminium and to the same Al-.45 % Cu alloy very slowly cooled from 400° C (15 days from 400 to 200° C). After this treatment, the copper is precipitated and the matrix according to the equilibrium diagram contains less than .05 % Cu. These two metals give just the scattering due to Compton effect and thermal agitation (Fig. 5). The excess scattering of the solid solution Al Cu is just equal to the Laue scattering.

2) But these examples of perfectly disordered solid solutions are rather exceptional. In most cases, the repartition of the soluted atoms is not random, either by a partial segregation or by a partial ordering.

It is well-known that in Al-Zn alloys, segregation of Zn into G.P. zones occurs immediately after quenching, even at very low temperatures. These zones can be dissolved by a reversion treatment (4 min at 200° C) and it was believed that in this state the atoms were randomly dispersed. But we have found that the scattering of reverted Al-4.5 % Zn alloy was twice the Laue scattering just after the reversion treatment. That means, according to Eq. 2, that Zn atoms are already grouped on the average in clusters of two atoms. At room temperature, the alloy is not stable and the scattering increases:after an hour the first G.P. zones are observed, the scattering is no more decreasing from zero angle but there is a maximum ('ring') at an angle of 3° 40'(Fig. 6). This evolution of the alloy cannot be detected by ordinary methods of X-Ray scattering measurement : the first change is sensible after one month of aging at room temperature.

On the other hand, we have found that the scattering of a Cu-10 o/o Au alloy gives a scattering smaller than the Laue scattering. That means that the repartition of the Au atoms is not quite random and that there is a tendancy to ordering : in the first shell of neighbours around an Au atom, there are less Au atoms than the random proportion. Of course the value of scattering at 0 angle alone is not sufficient to calculate the short range order coefficient, but it detects this very small difference with perfect disorder which would not be visible in a conventional scattering diagram.

3) Impurities in an ionic crystal

Single crystals of LiF with different impurity contents have been compared. The main impurity is known to be Mg and we have especially used the purest possible sample and a sample containing 100 p.p.m. of Mg. Fig. 7 gives the difference between the scattering of the two samples : thus Compton and thermal scatterings are eliminated with a satisfactory accuracy. The result is found 1) much too high to be due to isolated Mg^{++} ions dispersed in LiF lattice, 2) not constant but decreasing with angles. The conclusion is that the Mg^{++} impurities cannot be considered as point defects : they are probably grouped in such a way that there exist clusters of a few cells(about 10) in which the electronic density is different from the normal. But for the moment, we are not able to give a more precise model of these defects.

4) Radiation damage in LiF

The defects provoked by neutron irradiation in LiF which have been studied previously by X-Ray scattering are relatively large defects, condensation of vacancies or of interstitials. They occur for heavy irradiation doses and eventually subsequent annealings.But it is expected that the beginning of the process is the formation of isolated defects which may cluster when they are numerous enough and when the temperature of the crystal is sufficient to allow diffusion. Therefore we have studied the scattering of irradiated LiF crystals and here are the results of some preliminary experiments.

a) The effect of irradiation is sensible for doses above 10^{14} n/cm^2 (irradiation at pile temperature) whereas ordinary methods are insensitive up to doses of 10^{17} n/cm^2.

b) The scattering is not angle independent in the small angle region. Therefore the defects produced by neutron irradiation are not only vacancies and interstitials, but even for small radiation doses, there are already large defects.

Conclusion

These first experiments show what kind of information may be drawn from the measurements of weak X-Ray scatterings. They also give an idea of the sensitivity which can be reached.

Some improvements of the apparatus have been suggested by these experiments. It appeared necessary to vary the temperature of the specimen and especially to cool it down to liquid N_2 temperature; because of that one could make a better correction for thermal scattering and also the limit of sensitivity would be increased.

This method is able to supplement the other X-Ray methods in the study of solid solutions and radiation damages. An unexpected result has been found in the case of lithium fluoride containing a small amount of impurities, because the observed scattering is much higher than if the foreign ions were dispersed and substituted to normal ions in the undeformed lattice.

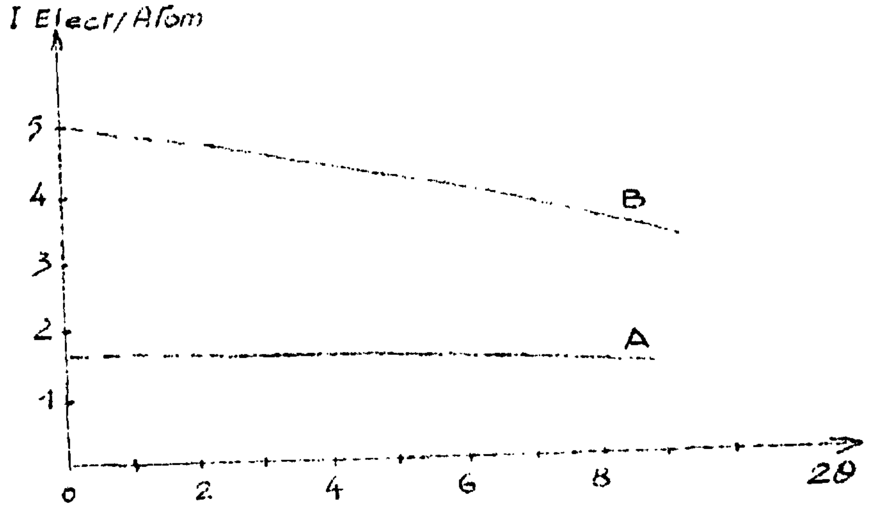


Fig. 1.- Scattering power per atom of 1 % vacancies in an aluminium crystal :
A) isolated vacancies,
B) vacancies grouped in clusters of 3.

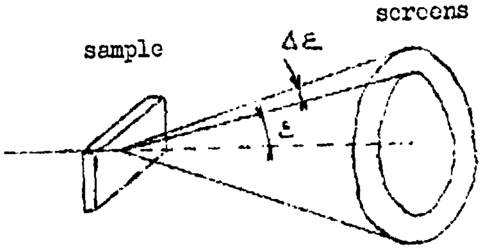


Fig. 2.- Annular slit limiting the scattered beam.

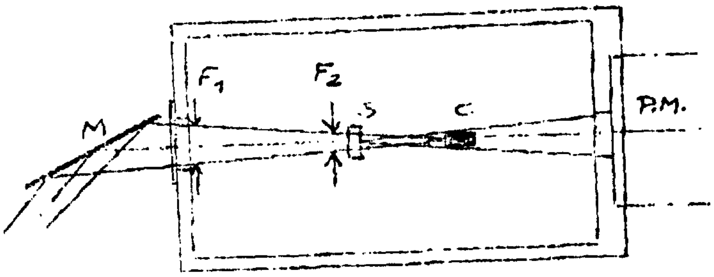
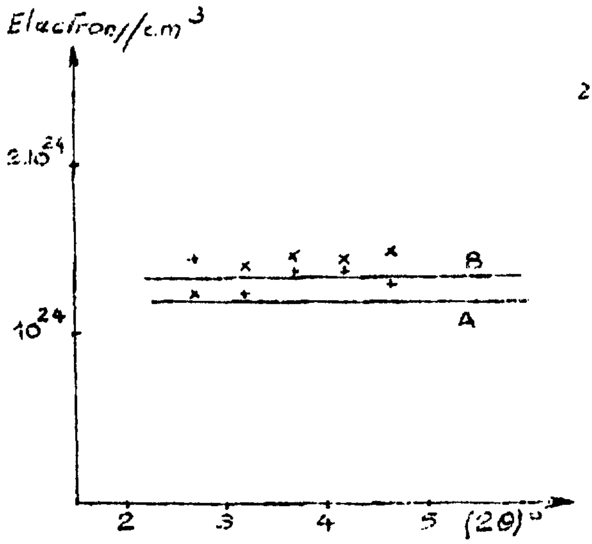
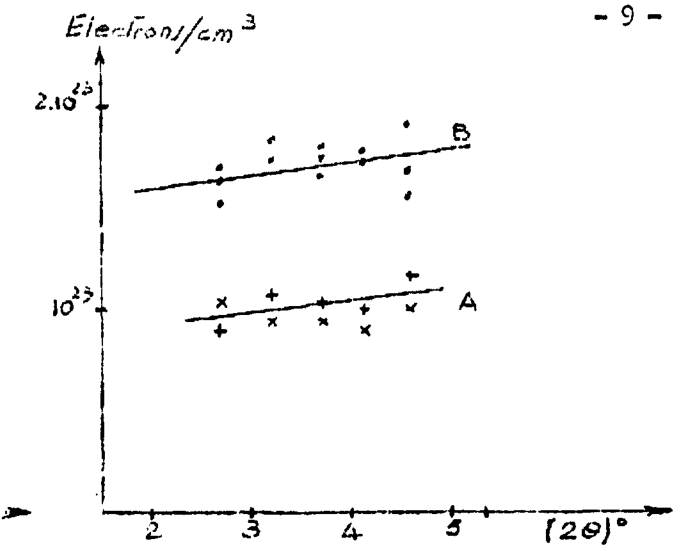


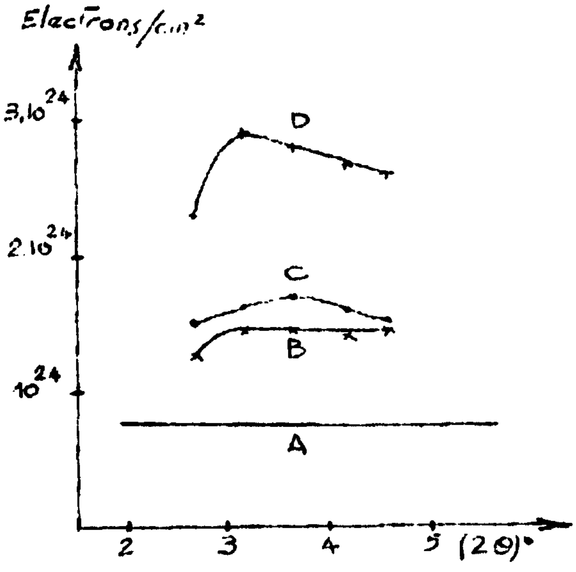
Fig. 3.- Scheme of the apparatus
S, sample,
C, beam catcher,
M, monochromator,
F_1 and F_2, slits.



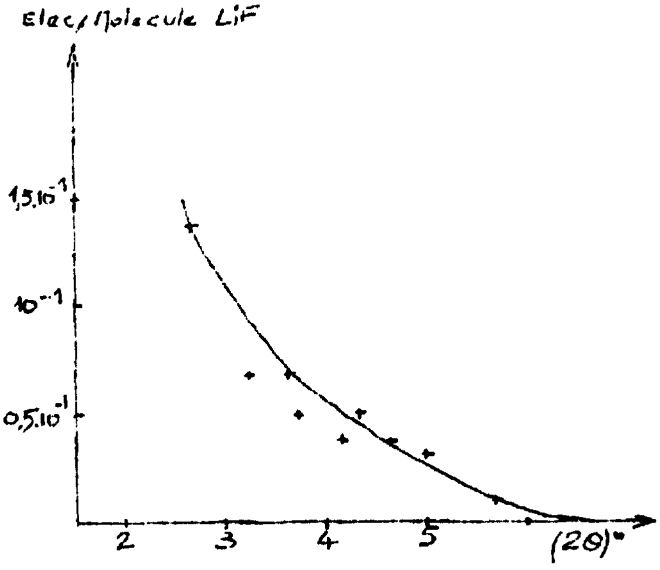
<u>Fig. 4</u>.- Scattering by a Al-6.4 % Ga alloy
Curve A : calculated Laue scattering,
Curve B : Laue scattering + Compton and thermal scattering



<u>Fig. 5</u>.- Scattering by Al-.45 % Cu alloy
Curve A : Compton and thermal scattering
Curve B : Laue scattering + Compton and thermal scattering
• experimental points for a quenched alloy,
× " " for a slowly cooled alloy.



<u>Fig. 6</u>.- Scattering by a Al-4.5 % Zn after reversion
Curve A : Theoretical Laue scattering,
Curve B : Experimental scattering immediately after reversion,
Curve C : Experimental scattering after 1 hour aging at room temperature,
Curve D : Experimental scattering after 24 hours at room temperature.



<u>Fig. 7</u>.- Scattering by LiF containing 100 p.p.m. Mg.
Difference between the scatterings of the impure and the pure Li F.

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